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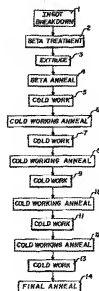
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Process for producing a thin-walled tubing from a zirconium-niobium alloy.

Thin-walled tubing of a zirconium-niobium alloy is fabricated by a process using a beta-quench prior to extrusion, the material being extruded at a temperature of 650 °C or lower and cold worked with annealing, between a plurality of cold working stages, effected at a temperature of below 650 °C, and the tubes then being subjected to a final anneal at a temperature below 600 °C. The resultant thin-walled tubing has a microstructure of homogeneously dispersed niobium particles of a size less than about 800 angstroms, with the tubing exhibiting excellent corrosion resistance.



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TITLE MODIFIED
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PROCESS FOR FABRICATING THIN-WALLED TUBING

This invention relates to a process for fabricating thin-walled tubing such as nuclear fuel cladding, from a zirconium-niobium alloy such that the alloys of the resultant products have a particular microstructure which enables the material to resist corrosion in high temperature aqueous environments.

Binary zirconium-niobium (Zr-Nb) alloys have been traditionally of interest to the nuclear industry because of their high strengths. It is this feature, in conjunction with reasonably good corrosion resistance, which ultimately led to the selection of the alloy of zirconium containing 2.5 per cent by weight niobium, as the standard pressure tube material for present generation Canadian Deuterium Uranium (CANDU) reactors. Although it was originally believed that the zirconium-niobium alloys had inferior resistance to irradiation enhanced corrosion relative to existing alloys, such as Zircaloy-2 or Zircaloy-4, it ultimately became apparent that they actually had superior in-pile corrosion properties when properly heat treated, as described by J. E. LeSurf, ASTM STP-458, p. 286. As a result of this finding, there has been increasing interest in zirconium-niobium alloys as potential fuel cladding materials in future generation, high performance, light water reactors.

At present, there is one major drawback which could prevent successful employment of zirconium-niobium

alloys as fuel cladding materials. This problem stems from the fact that superior corrosion resistance has been obtained only after application of the following multi-step processing sequence: 1) anneal at 850-950°C and water quench; 2) cold work to 10 to 30 per cent reduction (optional); and 3) anneal for approximately 24 hours at approximately 500°C. This processing is easily applied to the thick-walled pressure tubes for which it was developed, but cannot be applied to commercially produced thin-walled tubing with its inherently tight dimensional specifications and long lengths (~4 m), which causes problems relative to maintaining the shape of the tubing. It is thus necessary that an alternate processing system be adopted for the production of thin-walled tubing from zirconium-niobium alloys, for use as fuel cladding. Also, any such processing system must yield superior corrosion resistance and at the same time, be consistent with practices employed in the commercial production of fuel cladding.

We have found that zirconium-niobium alloys can be fabricated into thin-walled tubing, of about 0.040 inch or less in wall thickness, which exhibits excellent corrosion resistance, by a process that does not require extensively long final annealing times, by the use of relatively low temperature anneals between cold working steps and a final low temperature anneal. By using the processing techniques of the present invention, thin-walled tubing can be fabricated that has a microstructure where second phase beta-niobium particles are homogeneously dispersed in the zirconium matrix in extremely fine particle size to provide excellent corrosion resistance of the resultant article under both in-pile and out-of-pile conditions.

Accordingly, the present invention resides in a process for fabricating thin-walled tubing from a zirconium-niobium alloy containing from 1 to 2.5 per cent by weight niobium as homogeneously dispersed finely divided particles characterized by beta-treating a zirconium-niobium alloy billet containing from 1 to 2.5 per cent by

weight niobium; extruding said beta-treated billet at a temperature no higher than 650°C to form a tube shell; further deforming said tube shell by cold working the same in a plurality of cold working stages; annealing said tube shell, between each of said stages of cold working, at a temperature below 650°C; and final annealing the resultant tubing at a temperature below 600°C, so as to produce a microstructure of the material having niobium particles of a size below about 800 angstroms homogeneously dispersed therein.

The fabrication of thin-walled tubing from a zirconium-niobium alloy is effected according to the present invention with the production of tubing exhibiting excellent corrosion resistance and resistance to hydride formation.

Especially useful are zirconium alloys containing 1.0 per cent by weight and 2.5 per cent by weight niobium. The zirconium-niobium alloys may contain a minor amount, up to 0.5 per cent by weight of a third element, such as copper, iron, molybdenum, nickel, tungsten, vanadium and chromium. An example of such an alloy is one containing zirconium with 2.5 per cent niobium and 0.5 per cent copper.

In one embodiment of the invention, the alloys are first subjected to a beta-treatment by heating the alloy to from 950-1000°C and water-quenching the same to a temperature below the alpha + beta to alpha transus temperature. The billet is then prepared for extrusion by drilling an axial hole along the center line of the billet, machining the outside diameter to desired dimensions, and applying a lubricant to the surfaces of the billet. The billet diameter is then reduced by extrusion at a lower than conventional temperature, below 700°C, through a frustoconical die and over a mandrel. A beta-anneal of the extruded tube shell may then be effected, depending upon the alloy, by heating to from 850-1050°C, followed by rapid cooling. The billet may then be cold worked by pilgering,

at a source of primary fabrication, to reduce the wall thickness and outside diameter. This intermediate production is called a TREX (Tube Reduced Extrusion), which may then be sent to a tube mill for fabrication by cold working, intermediate low temperature annealing, and a final anneal under the fabricating steps of the present invention to produce the desired thin-walled tubing. In the formation of the thin-walled tubing, the material is preferably cold worked by pilgering, and 3 to 5 stages of cold working effected, preferably 3 to 4 stages.

The present invention produces thin-walled zirconium alloy tubing wherein the alloying elements are homogeneously dispersed throughout the zirconium in a finely divided state. The particles, homogeneously dispersed, are of an average particle size below 800 angstroms, and preferably the average particle size is below about 500 angstroms.

In order that the invention can be more clearly understood, convenient embodiments thereof will now be described, by way of example, with reference to the accompanying drawings in which:

Figure 1 is a flow diagram of a process for fabricating thin-walled tubing;

Figure 2 is a graph illustrating the superior corrosion resistance of the zirconium-niobium alloy containing 1 per cent niobium processed according to the flow diagram of Figure 1, as compared with reported corrosion resistance of such an alloy;

Figures 3A, B, C and D show transmission electron microscopy photomicrographs illustrating the typical precipitate distribution and size observed in a fully annealed tubing formed from a zirconium alloy containing 1.0 per cent by weight niobium and produced according to the flow diagram of Figure 1;

Figures 4A, B, C and D show transmission electron microscopy photomicrographs illustrating the typical precipitate distribution and size observed in a fully

annealed tubing formed from a zirconium alloy containing 2.5 per cent by weight niobium and produced according to the flow diagram of Figure 1; and

Figures 5A, B, C and D show transmission electron microscopy photomicrographs illustrating the typical precipitate distribution and size observed in a fully annealed tubing formed from a zirconium alloy containing 2.5 per cent by weight niobium and 0.5 per cent by weight copper and produced according to the flow diagram of Figure 1.

Referring to Figure 1, a niobium-containing zirconium alloy (A) ingot, containing 1.0 per cent by weight niobium and the balance zirconium, was conventionally broken down in billets of about six inches in diameter (Step 1). A six-inch diameter billet was then given a beta treatment, Step 2, which comprised holding the billet in a furnace at about 968-996°C (1775-1825°F) for about fifteen minutes and then water quenching the billet. At this point, the beta-treated billet was machined, bore-holed and inspected in preparation for extrusion. The hollow niobium-containing zirconium alloy billet was then heated to about 649°C (1200°F) and extruded (Step 3) to a hollow tube having an outside diameter of 2.5 inches and a wall thickness of 0.43 inch.

The extruded hollow tube was beta-annealed (Step 4) at 954°C (1750°F) for a period of fifteen minutes in preparation for a first cold working step (a pilgering reduction), (Step 5). The beta-annealed extrusion was pilgered in Step 5 to a TREX having an outside diameter of 1.75 inches and a wall thickness of 0.3 inch. The TREX was then annealed, (Step 6), at 500°C (932°F) for a period of 8 hours. Following the annealing of the TREX, the same was then cold pilgered to a tube shell having an outside diameter of 1.25 inches and a wall thickness of 0.16 inch, (Step 7). The tube shell was then further annealed and cold worked according to the following sequence. The tube shell was annealed, (Step 8), at about 524°C (975°F) for

7.5 hours and further cold pilgered, (Step 9), to reduce the tube shell to one having an outside diameter of 0.875 inch and a wall thickness of 0.085 inch. This tube shell was again annealed at about 524°C (975°F) for 7.5 hours, (Step 10). The annealed tube shell was again further cold pilgered, (Step 11), to give a tube shell having an outside diameter of 0.602 inch and a wall thickness of 0.045 inch. A further cold working anneal, (Step 12), was effected at about 524°C (975°F) for 7.5 hours and the tube shell finally cold pilgered, (Step 13), to give a tube having an outside diameter of 0.423 inch and a wall thickness of 0.025 inch. The tube was then subjected to a final anneal at about 427°C (800°F) for 4 hours, (Step 14).

A second niobium-containing alloy (B) ingot, containing 2.5 per cent by weight niobium and the balance zirconium, was treated according to the present process, the B composition ingot treated as was A, except for the following variations. An examination of the TREX indicated that the B composition had not received the correct beta-anneal and was, prior to Step 7, given a further, extra annealing at 580°C (1076°F) for a period of 8 hours. Also, the cold working anneal for the tubes formed from composition B were effected at about 580°C (1076°F) for 8 hours (rather than 524°C (975°F) for 7.5 hours as with A). The remaining treatment steps, including the final anneal were the same as those used with composition A.

A third niobium-containing alloy (C) ingot, containing 2.5 per cent by weight niobium, 0.5 per cent by weight copper, and the balance zirconium, was treated according to the present invention, the C composition ingot treated as was composition A through Step 5. The TREX was then annealed in Step 6 at 600°C (1112°F) for a period of 8 hours. When the cold working of Step 7 was attempted, transverse cracks appeared. The material was therefore subjected to an additional anneal for 3 hours at about 685°C (1265°F) and the material then subjected to Step 7 with successful pilgering. Also, the first cold working

anneal, Step 8, was carried out at about 593°C (1100°F) for a period of 8 hours. Subsequent cold working anneals were effected at about 580°C (1076°F), as with composition B. After the final cold work step, Step 13, the tube was
5 subjected to a final anneal, Step 14, for 7.5 hours at about 480°C (896°F).

Stress-relieved sections of tubing of compositions A, B and C, processed as described above, were corrosion tested in a static autoclave in 427°C, 10.3MPa
10 steam; and 360°C, 18.7MPa water; and compared with results of such corrosion testing of Zircaloy-4. The results of the corrosion tests are listed in Table I and demonstrate that zirconium-niobium alloys processed according to the present invention have corrosion resistance superior to
15 that of Zircaloy-4.

TABLE I
Static Autoclave Corrosion Data

Alloy	360°C			427°C		
	Exposure Time (days)	Weight Change (mg/cm ²)	Corrosion Rate (mg/dm ² /day)	Exposure Time (days)	Weight Change (mg/cm ²)	Corrosion Rate (mg/dm ² /day)
Zr - 1% Nb (A)	448	106.3	0.19	290	310.8	0.98
Zr - 2.5% Nb (B)	672	164.8	0.21	290	403.5	1.28
Zr - 2.5% Nb - 0.5% Cu (C)	672	111.8	0.17	290	182.7	0.53
Zircaloy-4	672	391.2	0.57	210	728.8	6.05

* Post-transition rate

- Further evidence of the corrosion resistance of the alloys treated according to the present invention is obtained by comparing the corrosion rates of the tubing of niobium-containing alloy containing 2.5 per cent by weight
- 5 niobium (alloy B) with published data which characterizes the corrosion rates of 2.5 per cent niobium-zirconium in the "heat treated" condition as described by J. E. LeSurf in "The Corrosion Behavior of 2.5 Nb Zirconium Alloy", Applications-Related Phenomenon for Zirconium and Its
- 10 Alloys, ASTM STP 458, American Society for Testing and Materials, 1969, pp. 286-300. This comparison is presented in Table II.

TABLE II

Post-Transition Rates of Tubing B Versus AECL Heat Treated Sheet (360°C)	
<u>Material</u>	Post-Transition Corrosion Rate (mg/dm ² /day)
B	0.21
20 *AECL Heat Treated:	
a) Quenched + Aged	0.43
b) Quenched + 10% Cold Worked + Aged	0.39
c) Quenched + 20% Cold Worked + Aged	0.13
d) Quenched + 30% Cold Worked + Aged	0.08
25 * Quenching Temperature = 880°C Aging Treatment = 24 hr @ 500°C	

- Additional evidence of the superior corrosion resistance of the alloys treated according to the present invention is provided by the post-irradiation examinations
- 30 performed on cladding of fuel rods. Two experimental Zr-Nb alloys were exposed in the BR-3 pressurized water reactor located in Mol, Belgium, for about seven and one-half months (at power). Five high-power fuel rods were removed

and sectioned at five elevations; one section at the peak power location; two sections at 90% power, above and below the peak power location; and two sections at 50% power near the ends. The minimum, maximum, and mean oxide thicknesses from those five sections are listed in Table III, in comparison with Zircaloy-4:

TABLE III

Oxide Film Thicknesses Measured on Fuel Rods
After BR-3 Cycle 3B Irradiation Test

10	<u>Alloy</u>	<u>Minimum (μm)</u>	<u>Maximum (μm)</u>	<u>Mean (μm)</u>
	Zr - 1% Nb (A)	1.962	3.875	3.011
	Zr - 2.5% Nb (B)	2.210	3.022	2.669
	Zircaloy-4	2.633	4.234	3.658

These examinations indicate that niobium-containing zirconium alloy tubes of the present invention have in-pile corrosion resistance superior to that of Zircaloy-4. This is a property which, in the past, has been attributed only to "heat treated" 2.5% Nb-zirconium alloys (see "The Effect of Aging and Irradiation on the Corrosion of Zr-2.5 wt % Nb", V. F. Urbanic, J. E. LeSurf and A. B. Johnson, Jr.: Corrosion 31 (1975) 15).

Further evidence of the superiority of the tubing prepared according to the present invention is illustrated in Figure 2 where two groups of corrosion data are presented for a zirconium alloy containing 1 per cent by weight niobium. The first group of data (dash lines: 350, 400 and 450°C) were reported for sheet material which was fabricated via standard Russian processing techniques (see A. A. Kiselev, et al., AECL-1724, 1963). The second group of data (solid lines: 360 and 427°C) were obtained from tubing processed according to the present invention. The superiority of the present tubing is demonstrated by the fact

that the same exhibits lower weight gains at 360 and 427°C than the Russian material does, even though the latter was exposed at lower corrosion temperatures 350 and 400°C respectively.

- 5 The present processing provides uniform distribution of very fine precipitate particles in the microstructure of niobium-containing zirconium alloys. The microstructure of the fully annealed tubing is illustrated in Figures 3A, B, C and D for composition "A"; 4A, B, C and
10 D for composition "B"; and 5A, B, C and D for composition "C". Because of the fine particle sizes obtained, transmission electron micrographs (TEM) were taken. In deformed materials, diffraction effects from grain boundaries and dislocations interfere with particle resolution. There-
15 fore, the study of particle dispersions was carried out on fully annealed, final tubing. The final annealing cycle for A was 8 hours at 500°C (932°F), and for B and C was 8 hours at 600°C (1112°F). Results of the characterization of the particle distribution in the annealed material are
20 given in Table IV as follows:

TABLE IV

Data on Particle Size Distributions
In Annealed Product Tubing

25	Alloy	Average Diameter	Number Density/cm ³
		(Angstroms)	
	A	230	11 x 10 ¹⁴
	B	420	12 x 10 ¹⁴
	C	450	8 x 10 ¹⁴

- 30 The observed precipitate sizes and number densities represent relatively fine dispersions. This is evident when comparing the same to the average diameter in the range of 3000 Angstroms of particle sizes in a conventionally processed Zircaloy-4 alloy.

CLAIMS:

1. A process for fabricating thin-walled tubing from a zirconium-niobium alloy containing from 1 to 2.5 per cent by weight niobium as homogeneously dispersed finely divided particles characterized by beta-treating a
5 zirconium-niobium alloy billet containing from 1 to 2.5 per cent by weight niobium; extruding said beta-treated billet at a temperature no higher than 650°C to form a tube shell; further deforming said tube shell by cold working the same in a plurality of cold working stages; annealing said tube
10 shell, between each of said stages of cold working, at a temperature below 650°C; and final annealing the resultant tubing at a temperature below 600°C, so as to produce a microstructure of the material having niobium particles of a size below about 800 angstroms homogeneously dispersed
15 therein.
2. A process according to claim 1, characterized in that the zirconium-niobium alloy contains 1 or 2.5 per cent by weight of niobium.
3. A process according to claim 2, characterized
20 in that the annealing of the tube shell is at a temperature of from 500-600°C.
4. A process according to claim 3, characterized in that the annealing of the tube shell is at a temperature of about 524°C for a period of about 7.5 hours.

5. A process according to any of claims 1 to 4, characterized in that the final anneal is at a temperature below 500°C.

5 6. A process according to claim 5, characterized in that the final anneal is at a temperature of about 427°C for a period of about 4 hours.

7. A process according to any of claims 1 to 6, characterized in that following the extruding and prior to the further deforming, the tube shell is beta-annealed by
10 heating the same at a temperature in the range of 850-1050°C and rapidly cooling the same.

8. A process according to any of claims 1 to 7, characterized in that the zirconium-niobium alloy contains up to 0.5 per cent by weight of copper, iron, molybdenum,
15 nickel, tungsten, vanadium or chromium as a third element.

9. A process according to claim 8, characterized in that the zirconium-niobium alloy contains 2.5 per cent by weight niobium and 0.5 per cent by weight copper, and said final anneal is at a temperature of about 480°C for a
20 period of about 7.5 hours.

10. A process according to any of claims 1 to 9, characterized in that the further deforming of the tube shell is effected in three to five stages.

11. A process according to claim 10, characterized
25 ized in that the further deforming of the tube shell is by pilgering the same.

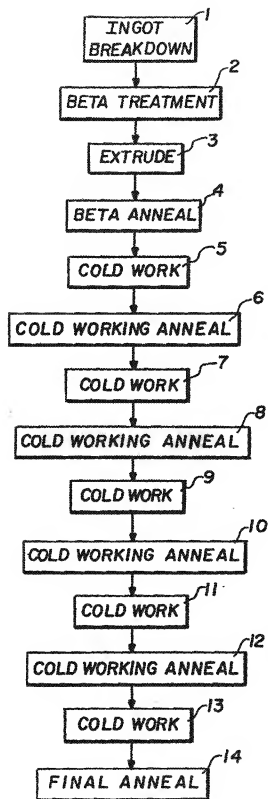
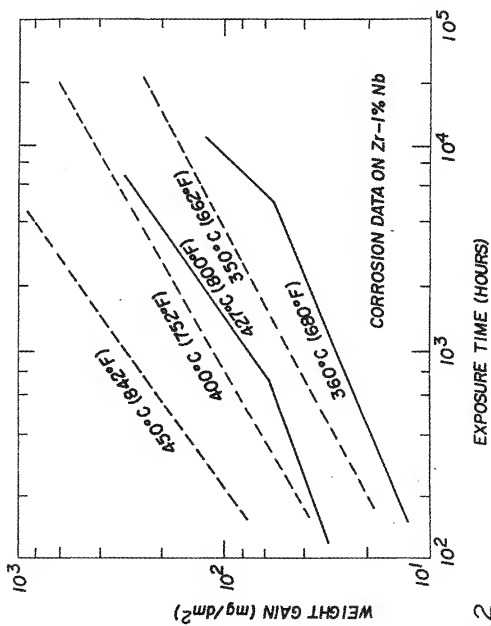


FIG. 1



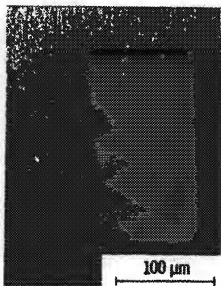


FIG. 3A

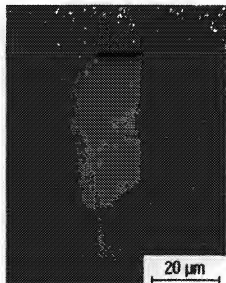


FIG. 3B

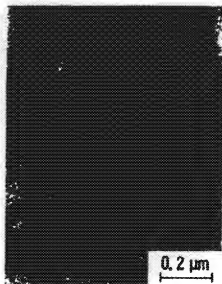


FIG. 3C



FIG. 3D



FIG. 4A



FIG. 4B



FIG. 4C

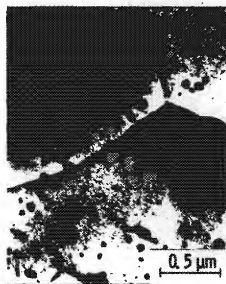


FIG. 4D

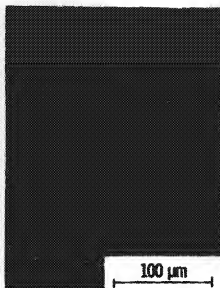


FIG. 5A



FIG. 5B



FIG. 5C

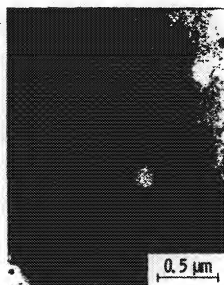


FIG. 5D